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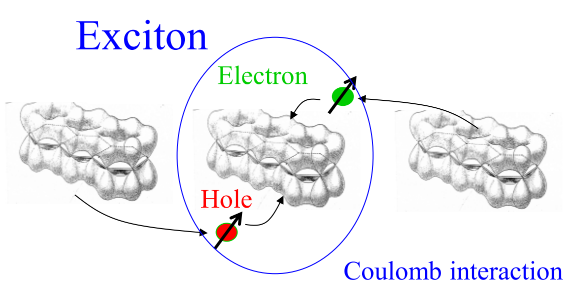
Advanced Course on

ORGANIC ELECTRONICS
Principles, devices and applications

Light generation: principles of OLED

Marco Sampietro

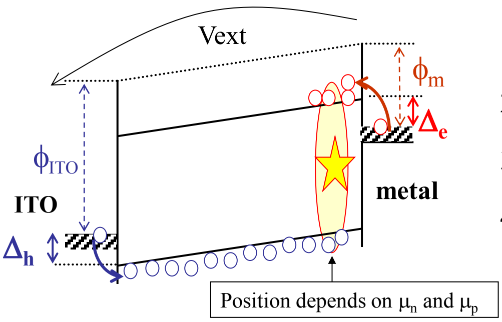
ORGANIC LED



EXCITON
neutral excited entity (molecule)
(presence of e^- - h^+ couple)

Organic materials	Silicon
⇩	⇩
ε small (2.5)	ε big (11)
⇩	⇩
tightly bound excitons (molecular excitations)	lousely bound excitons

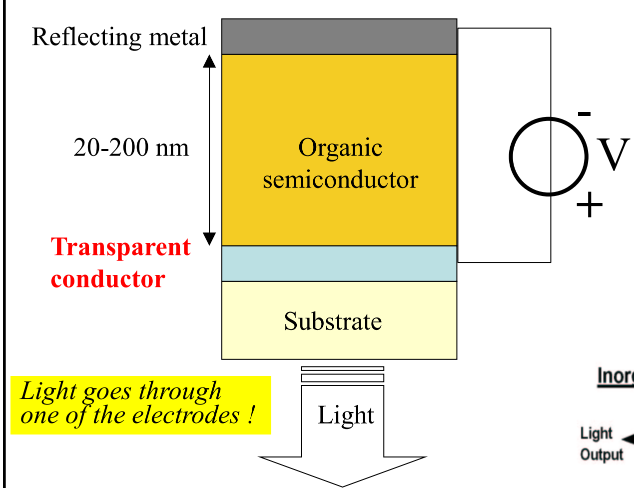
ORGANIC LED

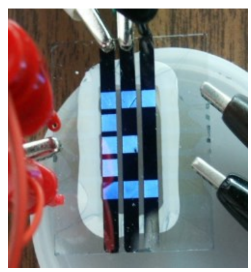


1. Charge injection
2. Transport
3. Exciton formation
4. Radiative recombination

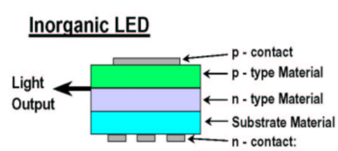
C.W.Tang et al. "LED on organic crystals" APL 51, 1987, 913-915 .H.Burroughes et al. "LED based on polymers" Nature 347 (1990) 539-541

ORGANIC LED

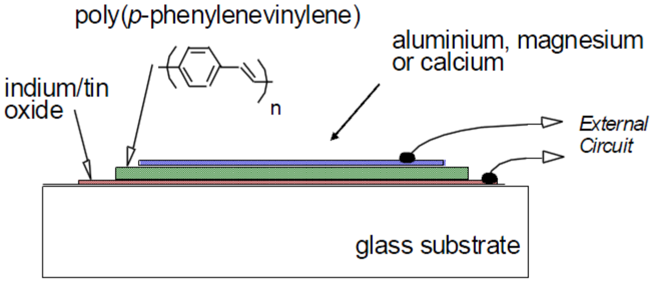




Collaborazione TESEO (~2002)



First layered OLED – Polymers



Burroughes et al.
Nature, **347**, 539 (1990) US patent 5,247,190

… a STEP forward of 25 YEARS

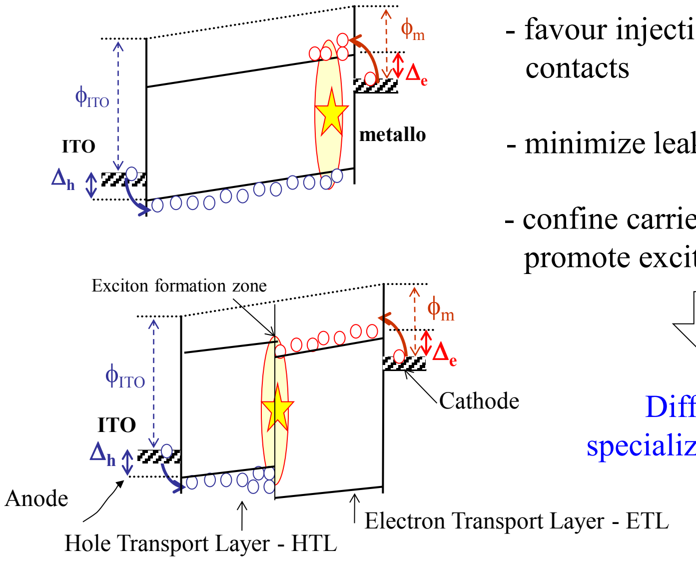
State of the art (6 Sept 2013)

77-inch Ultra HD curved OLED TV – LG Display

- @ IFA Consumer Electronics (Berlin)

- This new product has a 4K Ultra HD resolution - four times the number of pixels than a standard 1080p HD would have.

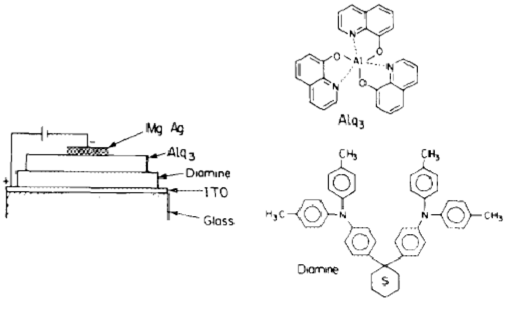
RADIATIVE RECOMBINATION



- favour injection from contacts
- minimize leakage current
- confine carriers in space to promote exciton formation

Different & specialized materials

First layered OLED – Small molecules

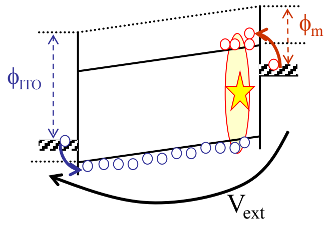


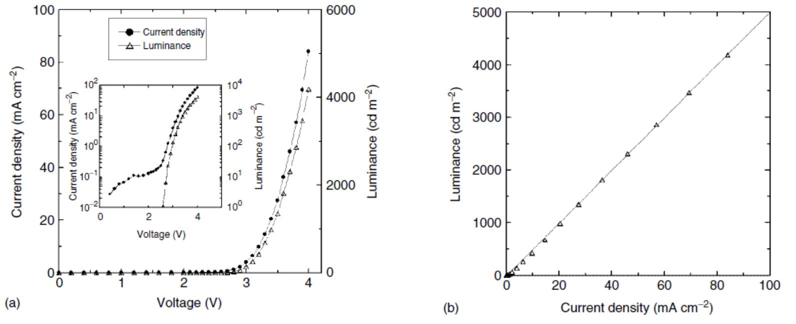
Ching Tang and Stephen van Slyke

Appl. Phys. Lett. **51**, 913 (1987)

- Electron transport through Alq_3
- Hole transport though triphenylamine
- Electron-hole capture at heterojunction

CHARACTERISTIC CURVES





ELETTROLUMINESCENCE EFFICIENCY

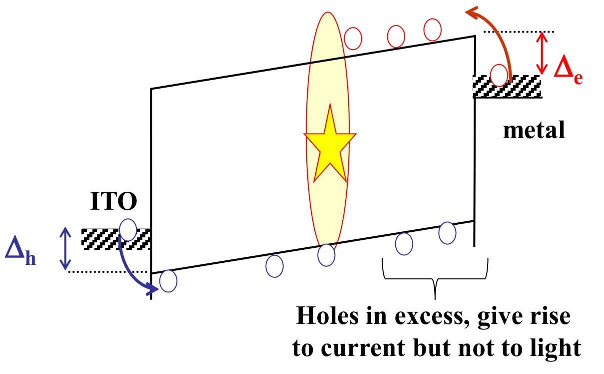
Loss mechanisms
(limiting devices efficiency):

- Charge un-balance (γ)
- Fraction of excitons that decay radiatively (r_{st})
- quantum efficiency of the emissive molecule (η_{pl})
- Light extraction ($\eta_{coupling}$)

These factors can be combined to define the external quantum efficiency, EQE, as:

$$\eta_{ext} = \gamma \cdot r_{st} \cdot \eta_{PL} \cdot \eta_{coupling} \qquad \frac{\text{n. of emitted photons}}{\text{n. of injected charges}}$$

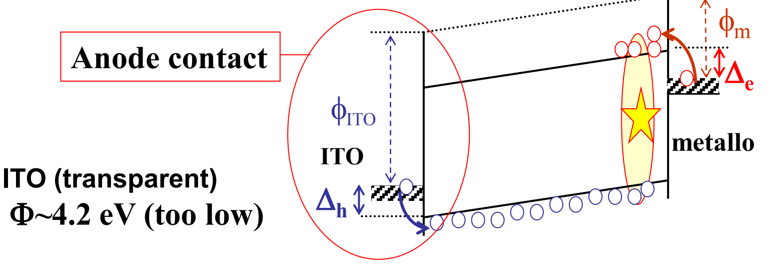
CHARGE UN-BALANCE (I)



Equivalent barriers for holes and electrons are beneficial

BARRIER MINIMIZATION (Anode)

Hole injection (1)



•O_2 plasma treatment
(~ 4 min at 50mW/cm^2, Φ~4.7 eV) → D.J.Milliron et al., JAP 87, 572, 2000

BARRIER MINIMIZATION (Anode)

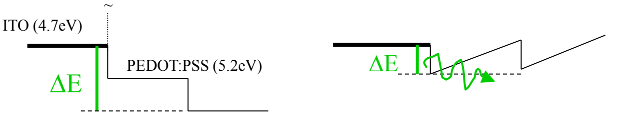
- **Thin conductive layer between ITO and polymer (smooth surface, barrier for ion diffusion→lifetime)**

•Poly(aniline) or poly(thiophene) - MEH-PPV

A.J.Heeger et al., Synt.Met. 67, 23, 1994
Y.Scott et al., Synt.Met., 85, 1197, 1997

•PEDOT:PSS, best with PFO

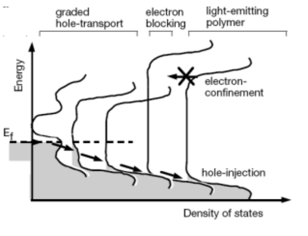
A.Elschner et al, Synt.Met.111,139,2000
L.B.Groendaal et al., Adv.Mat. 12, 481, 2000
A.J. Campbell et al., JAP 89, 3343, 2001



•Graded barrier for hole injection (PEDOT:PSS complexed with poly-p-xylylee-a-tetra-hydrothiophenum)

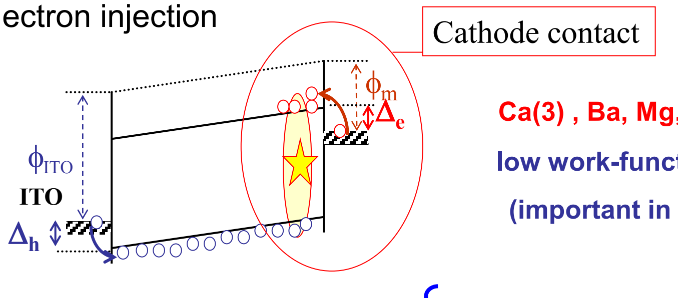
Efficiency 50 times greater than standard PEDOT:PSS

P.K.H.Ho et al.,Nature,404,481,2000



BARRIER MINIMIZATION (Cathode)

Electron injection



Ca(3) , Ba, Mg, Yb(2.6), Li

low work-function metals

(important in blue LED)

1. Insertion of additional layers at the cathode side (Alkane-thiol in MEH-PPV)

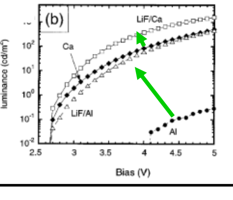
I. H. Campbell et al., *Phys. Rev. B* 54, 14 321, 1996

- **Local electric field increase**
- **Tunneling increase**
- **Barrier tuning over a 1 eV range**

2.Use of fluorides, oxides, sulphides

E.g. LiF, CsF capped with a thick Al

T. M. Brown et al., *APL* 79, 174, 2001
T.M.Brown JAP 93, 6159 (2003)

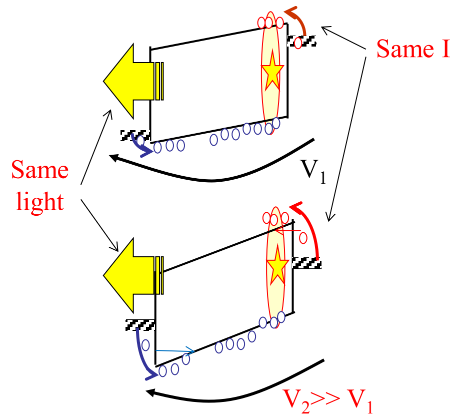


Luminance increase with fluorides insertion

BARRIER MINIMISATION

Small barriers increase power efficiency

$$P_{eff} \div \eta_{ext} \cdot \frac{h\nu}{eV}$$



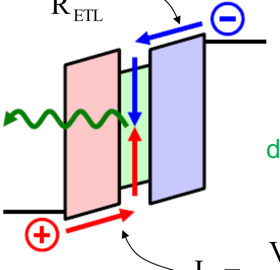
CHARGE UN-BALANCE (II)

Back to : $\eta_{ext} = \gamma \cdot r_{st} \cdot \eta_{PL} \cdot \eta_{coupling}$

Probability that e^-&h^+ meet and form excitons

If barrier is small (no injection limit) current depends on transport layers resistance

$$I_n = \frac{V}{R_{ETL}}$$



$$I_p = \frac{V}{R_{HTL}}$$

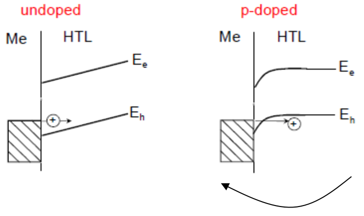
$$R_{ETL} = \frac{1}{q\mu_n n} \cdot \frac{L}{S}$$

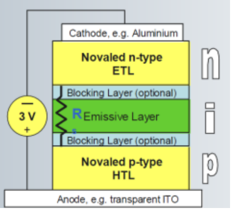
Un-matched mobilities produce different electrons and holes fluxes

$$R_{HTL} = \frac{1}{q\mu_p p} \cdot \frac{L}{S}$$

It is important to choose suitable HTL and ETL

OLED with Doped Transport Layers : reduction of voltage





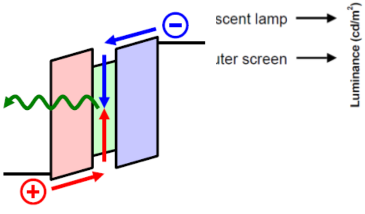
http://www.novaled.com
Adv. Funct. Mater. 11 310 (2001)
Appl. Phys. Lett. 85 3911 (2004)
J. Soc. Inf. Display 13 393 (2005)
Chem. Rev. 4 133 (2007)

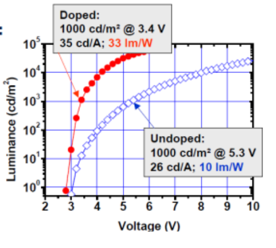
Low device resistance

→ Low voltage drop

Better injection irrespective of contact metal (small depleted region)

Organic doping - an Example:
doped vs. undoped green OLED





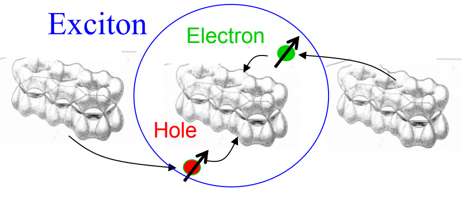
$$P_{eff} \div \eta_{ext} \cdot \frac{h\nu}{eV}$$

V close to thermodynamic limit (e.g. 2.5V for blue)

SINGLET - TRIPLET RATIO

$$\eta_{ext} = \gamma \cdot r_{st} \cdot r_{EL} \cdot \eta_{coupling}$$

η_{EL}

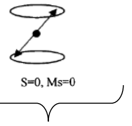


e⁻ and h⁺ have spin (spin number ½).

Capture of e⁻ and h⁺ (Exciton formation) is spin-independent.

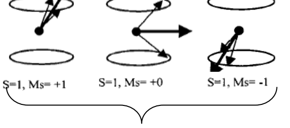
Spins can be up or down, and can precess in or out of phase (4 possible permutations)

Singlets Excitons
(Total spin angular mom. = 0)



25 %

Triplets Excitons
(Total spin angular mom.= 1)



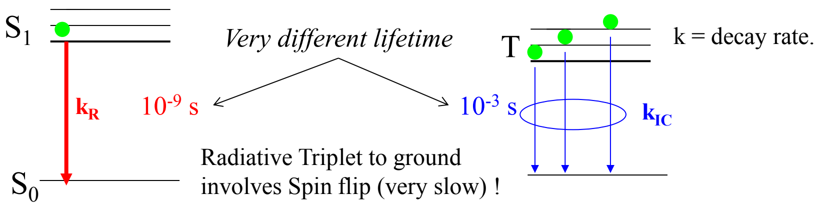
75 %

Spin momentum should be conserved for radiative decay

FLUORESCENCE

25% Excitons with SINGLET character …

75% Excitons with TRIPLET character



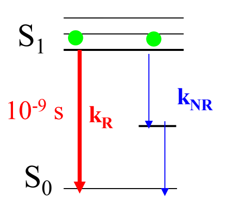
… undergo radiative recombination (FLUORESCENCE)

NON radiative recombination

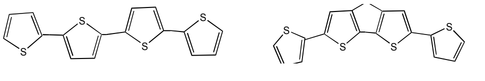
In conventional fluorescent devices only singlet excitons (25%) recombine radiatively (75% goes into heat) at best **$\eta_{EL}|_{max} = 25\%$**

FLUORESCENCE LOSS

25% Excitons with SINGLET character — Initial situation



T4 T4B



	η_{EL}	τ (ns)	K_R	K_{NR}	η_T	K_{ISC}
T4	0.17	0.41	0.41	2.02	0.71	1.72
T4B	0.24	0.53	0.45	1.43	0.60	1.1

$K_R = \eta_{EL}/\tau$

T.Benincori et al. Phys. Rev. B 58, 9092 (1998)

Torsional relaxation introduces NON RADIATIVE recombination channels

LESS than 25% of excitons recombine radiatively **$\eta_{EL} < 25\%$**

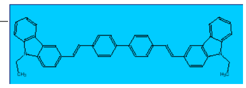
Fluorescent emitters : examples

Table 1. Typical RGBW electroluminescence characteristics of SM-OLEDs based on fluorescent materials

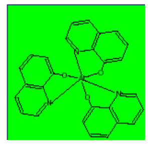
Colour	Material	CIE x	CIE y	Efficiencies η_{ext} (%)	Efficiencies cd A^{-1}	Efficiencies lm W^{-1}
Blue	DSA-doped DPVBi	–	–	2.4	2.8	1.5
	BCzVB-doped CBP	0.15	0.16	2.6	3.5	–
	BCzVB-doped DPVBi	0.15	0.14	5.7	7.0	–
	DPVBi	0.16	0.14	–	1.8	1.1
	SAlq	0.17	0.19	3.0	6.9	2.0
Green	Alq_3	–	–	1.3	–	–
	QA-doped Alq_3	–	–	3.0	–	–
	coumarin-doped Alq_3	–	–	2.5	–	–
	Alq_3	0.39	0.55	–	2.6	–
	DMQA-doped Alq_3	0.39	0.59	–	7.3	–
Red	DCM-doped Alq_3	–	–	–	–	–
	DCJTB-doped Alq_3	0.64	0.36	–	2.5	0.9
	DCJTB- and rubrene-doped Alq_3	0.64	0.35	–	3.2	1.2
White	DPVBi/Alq_3	0.28	0.34	–	4.7	2.9
	DCJTB-doped SAlq	0.33	0.39	2.0	6.6	2.3
	PAP-ph + Alq3 + DCM-doped Alq3	0.35	0.34	1.9	3.9	2.0

Alq_3 = tris(8-hydroxyquinolato)aluminium(III).
BCzVB = 4, 4′-(bis(9-ethyl-3-carbazovinylene)-1,1′-phenyl.
CBP = 4, 4′-*N*, *N*′-dicarbazole-biphenyl.
DCJTB = 4-(dicyanomethylene)-2-t-butyl-6(1,1,7,7-tetramethyljulolidyl-9-enyl)-4H-pyran.
DCM = 4-(dicyanomethylene)-2-methyl-6-(*p*-dimethylaminostyryl)-4H-pyran.
DMQA = *N*, *N*′-dimethylquinacridone.
DPVBi = 4, 4′-bis(2,2′-diphenylvinyl)-1,1′-biphenyl.
DSA = distyrylarylene.
PAP-ph = 1,7-diphenyl-4-biphenyl-3,5-dimethyl-1,7-dihydrodipyrazolo[3,4-b;4′, 3′-e]pyridine.
QA = quinacridone.
SAlq = bis(2-methyl-8-quinolato)-(triphenylsiloxy)aluminium(III).

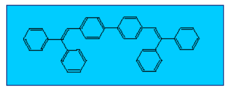
BCzVBi



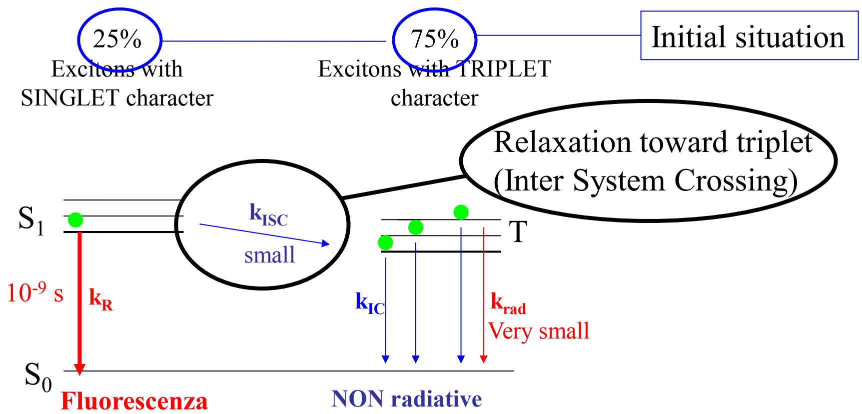
ALQ_3



DPVBi



SINGLET to TRIPLET LOSS



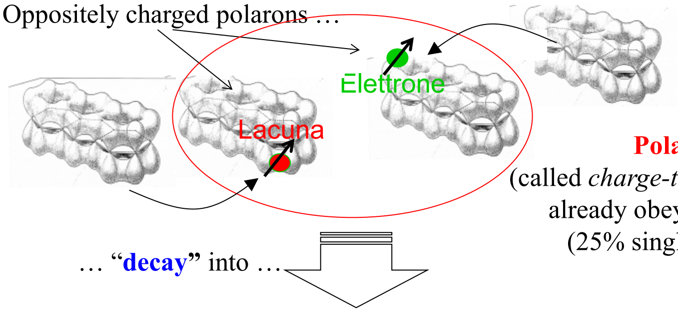
Another reason for

LESS than 25% of excitons recombine radiatively

$\eta_{EL} < 25\%$

FROM CHARGED POLARON TO NEUTRAL EXCITON

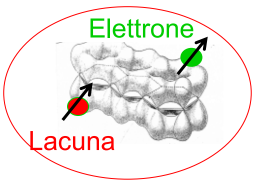
Oppositely charged polarons …



Polaron pair
(called *charge-transfer exciton-CT*),
already obey to spin statistics
(25% singlet, 75% triplet)

… "**decay**" into …

… singlet or triplet
neutral exciton



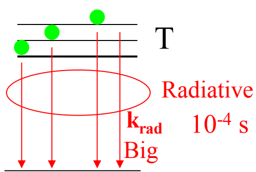
If **decay is fast** (faster than any other process affecting the intermediate CT) spin statistics is mantained :

CT singlet $\rightarrow$ Exc. Singlet 25%
CT triplet $\rightarrow$ Exc. Triplet 75%

J.L.Bredas et al. , Chem. Rev. 2004, 104, 4971-5003

This is the case of small molecules

TRIPLETS MAY BE MADE RADIATIVE !



Phosphorescence

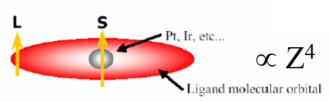
If decay **is slow**, triplets may have time to feel "spin-orbit coupling"
(electromagnetic interaction between the electron's spin and the magnetic field generated by the electron's orbit around the nucleus)

⇩

spin flip

⇩

radiative recombination



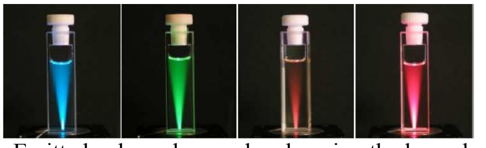
$\propto Z^4$

Molecules containing heavy atoms
(organometallic complexes with Ir, Pt)
show large spin-orbit coupling

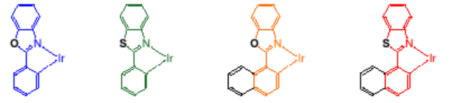
In principle, 100% of excitons can recombine radiatively

$\eta_{EL}|_{max}$ **= 100%**

Triplet harvesters : Iridium complexes



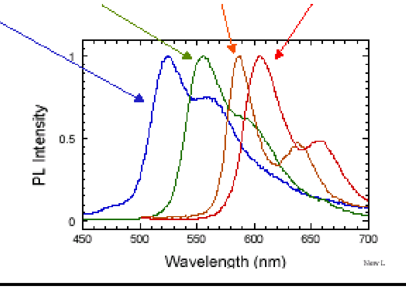
Emitted colour changes by changing the legand



Long exciton diffusion range (because of long lifetimes)

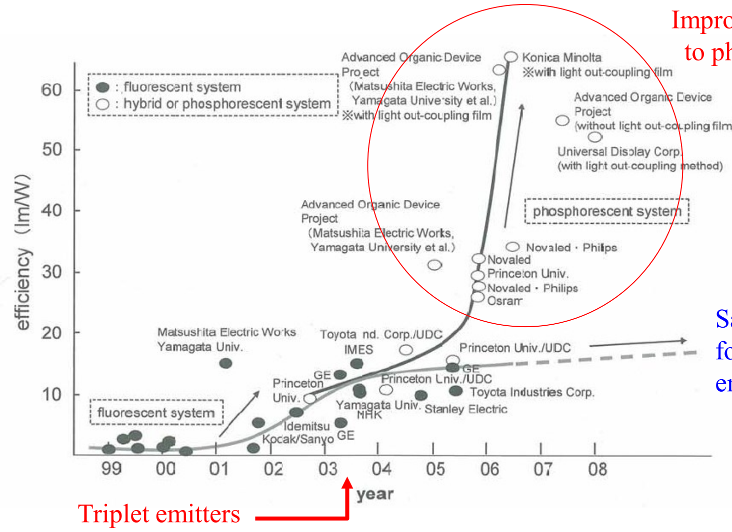
>140 nm compared to ~10-20 nm for singlets.

Exciton confinement layers needed to prevent excitons from crossing the whole active layer and decay non-radiatively at the electrodes.



EFFICIENCY IMPROVEMENT

Improvement thanks to phosphorescent emitters

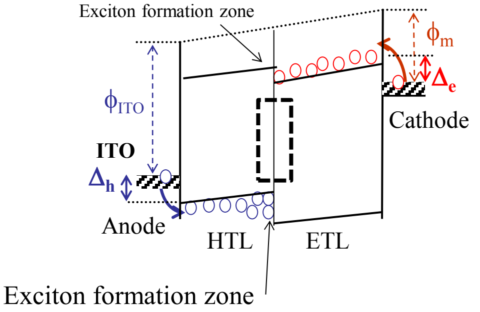


Saturated trend for fluorescent emitters

Triplet emitters

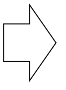
MATRIX of TRANSPORTER and EMITTER

A WAY TO IMPROVE EFFICIENCY



Different & specialized materials

Exciton may better be formed on a material different from the Emitter



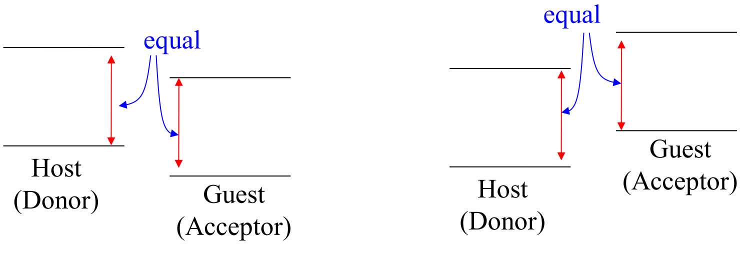
Exciton transfer:
Exciton, generated on one material (matrix, host, donor), transfers onto another material (guest, dye, acceptor) having better emissive properties

First group to use green phosphorescent dye to increase efficiency has been M. A. Baldo et al., *Nature* 395, 151 (1998), then V. Cleave et al., *Adv. Mater.* 13, 44, 2001

EXCITON TRANSFER : FÖSTER type

Dipole-dipole coupling of the donor and acceptor molecules.

Energy levels should be resonant.
Spectral superposition between host emission and dye absorption

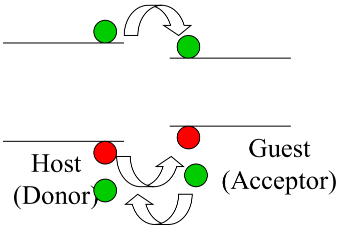


It is a "long" range interaction (up to 100 Å).
Mainly singlet excitons and triplet spin-orbit mediated.

The best transfer efficiency is obtained on molecoles with transition moments parallel and colinears

EXCITON TRANSFER : DEXTER type

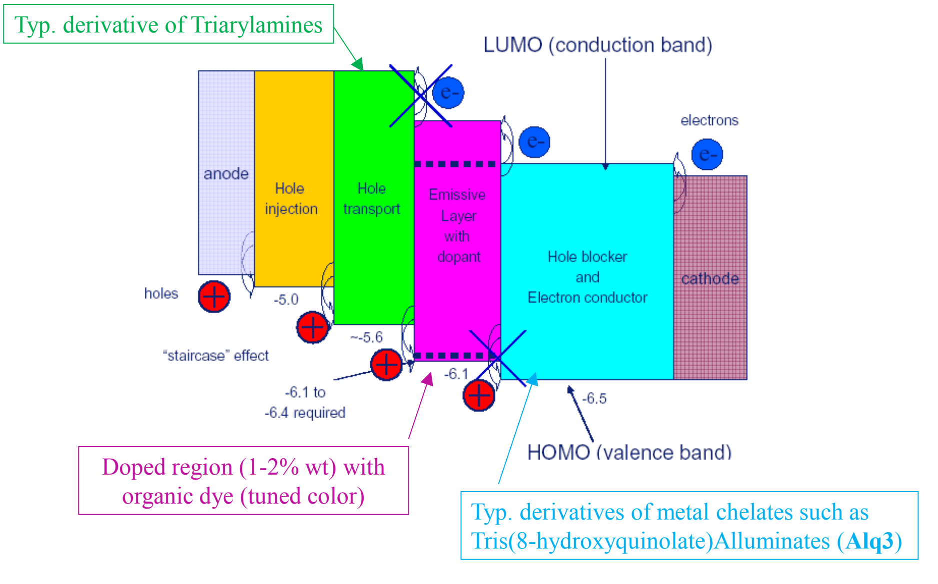
Simultaneous exchange of electrons btwn D and A molecules.



- emission shifts to the red
- auto absorption is minimum

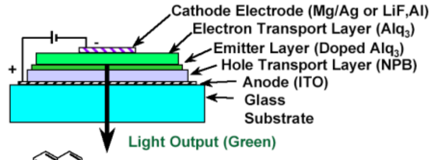
"Short" range (< 10 Å).
Possibile both for singlet and Triplet excitons.

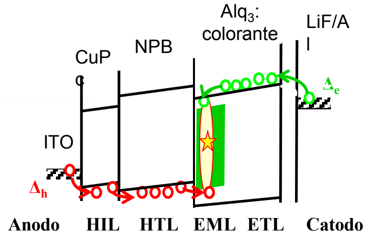
… in summary.

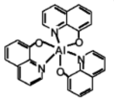


Layered OLED – Small molecules (1990)

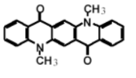
Brevetto Kodak



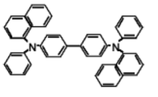




Electron Transport Layer Material - Alq_3



Dopant - DMQA
DiMetil QuinAcridone

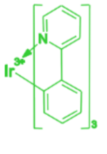


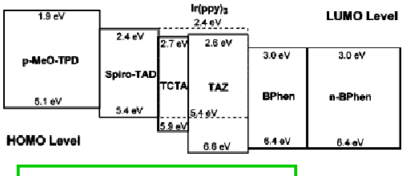
Hole Transport Layer Material - NPB
Naftalene Phenil Benzidina

Thickness of single layers : from 20 to 80 nm

Layered OLED – Polymers (2004)

2 breakthrough :
- doping of transport layers
- triplet emission



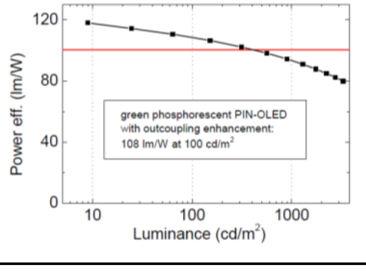


Iridium green triplet emitter

100 lm/W at 100 cd/m^2
(@2.7V drive voltage)

70 lm/W at 4000 cd/m^2

19 % external quantum efficiency



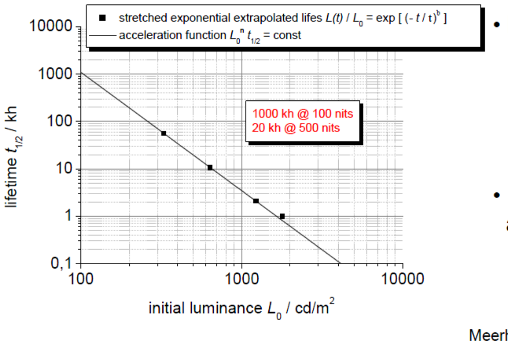
For comparison:

light bulb	15 lm/W
fluorescent tube	80 lm/W
halogen lamp	20 lm/W
white LED	60 lm/W

Karl Leo et al. , APL 85, 17 (2004)

Layered OLED – Polymers (2006)

Red OLED
using doping technology + triplet emitter + very stable material combinations



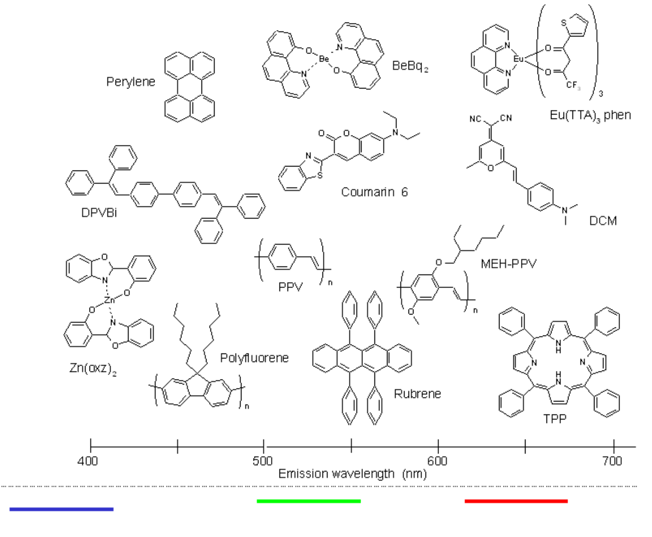
- high efficiencies reached:
  - 13 % external quantum efficiency
  - 12 cd/A deep red (0.68; 0.32)
  - low voltage: 2.5V for 100 cd/m²
  - --> high power efficiency
- Long lifetime, defined by device architecture and materials choice
  - up to 10^6 h @ 100 cd/m²

Meerheim, Walzer, Pfeiffer, Leo, APL 2006 (submitted)

Small molecules (SM-OLED) and polymers (PLED)

- Vacuum deposited (dry)
- Easier layer engineering

Solution deposited (wet)



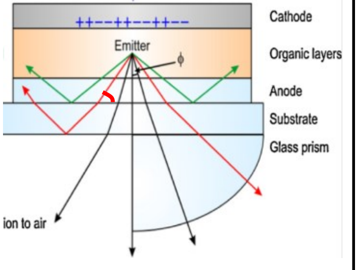
Optical output coupling

$$\eta_{ext} = \gamma \cdot r_{st} \cdot \eta_{PL} \cdot \eta_{coupling}$$

Is related to the extraction of the light toward the external environment

Mismatch between refractive index of EL layer and air→Total reflection for $\theta > \theta_c$ (critical angle) → Light is trapped

E.g.: $n_{EL} = 1.7$ → $\theta_c = 36°$



Simple expressions (from Snell's law)

•If one side is a prefect reflector and the emission is isotropic (molecules):

$$\eta_{coupling} \approx 0.5/n^2$$

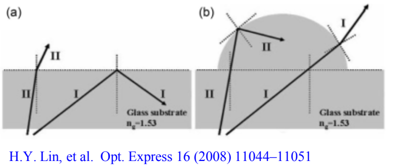
Typical values :

η = 17% for isotropic emission !!

(The remaining 83% of the photons are trapped in organic and substrate modes)

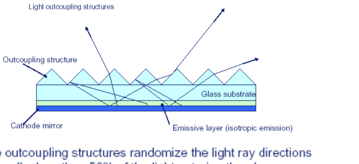
How to increase $\eta_{coupling}$?

Microlens arrays

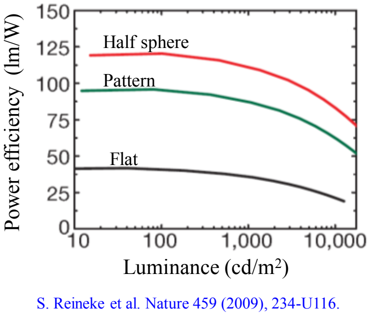


H.Y. Lin, et al. Opt. Express 16 (2008) 11044–11051

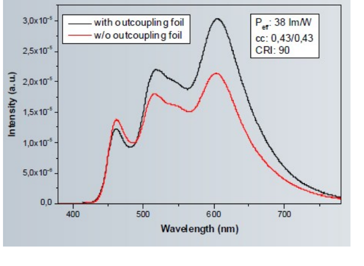
Textured surface



- The outcoupling structures randomize the light ray directions
- Normally, less than 50% of the light entering the glass can escape
- Optimised systems can increase this figure to about 80%



S. Reineke et al. Nature 459 (2009), 234-U116.



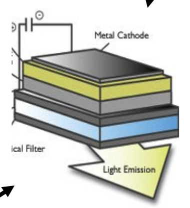
Summary of OLED characteristics

Brightness
10.000 cd/m²
(400 cd/m²)

All colors

Efficiency
> 40 lm/W
(2 lm/W)

Lifetime
> 10.000 h



Viewing angle
>160°
(60° - 150°)

Low voltage
< 10 V
(Backlight!)

Contrast
~∞

Thin & lightweight
Deposition

Time response
< µs
(16 ms)

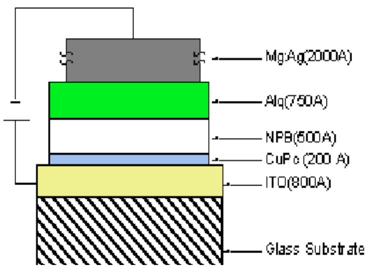
Scalable emissive area
from µm to cm

Temperature
-80°C / 80°C
(0°C / 40°C)

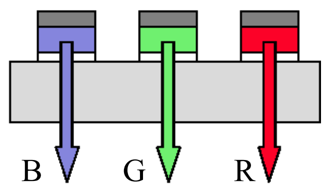
(AMLCD- Langfelder)

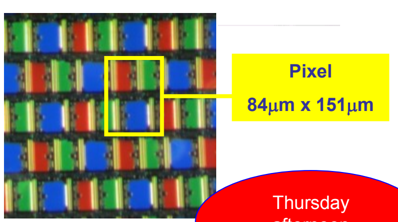
- Colors covers almost 85% of NTSC color spectrum standard

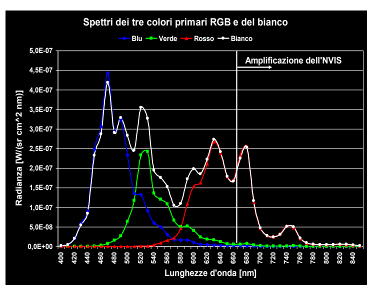
Multi PIXEL - SCREENS



SINGLE MOLECOLE







Thursday
afternoon
Marco Sampietro

Politecnico di Milano e Logic Spa

Universal Display Corporation

Ewing, New Jersey (S. Forrest)

www.universaldisplay.com

Developing a range of product and is floated on the NASDAQ ("PANL")

- PHOLED (Phosphorescent LEDs)

- TOLEDs (Transparent, top-emitting, stacked LEDs based on the TOLED concept)

- FOLED (Flexible OLEDs)

- WOLEDs (White OLEDs)